

A Refinement of the Crystal Structure of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$

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(January 28, 1970)

The crystal structure of synthetic $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ has been refined using 1231 unique x-ray diffraction data collected by the peak height method on a diffractometer. $R=0.034$. The unit cell is $a=6.474(2)$, $b=10.724(3)$ and $c=5.259(2)$ Å with $z=4$ and space group $\text{P2}_1\text{ab}$. The calculated density is the same as the observed density, $2.26 \text{ g} \cdot \text{cm}^{-3}$. The structure contains sheets of CO_3^{2-} ions bonded to Na^+ ions and water molecules roughly halfway between the sheets. Each CO_3^{2-} bonds edge-wise to both Na^+ ions. The Na^+ ions have irregular but similar coordinations of seven neighbors. Each water molecule is bonded to both Na^+ ions and forms hydrogen bonds to both neighboring CO_3^{2-} layers.

Key words: Crystal structure; hydrated carbonates; hydrogen bonding; sodium carbonate; thermonatrite; x-ray diffraction.

1. Introduction

The crystal structure of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ was determined except for the hydrogen positions, by Harper [1]¹ in 1936 using qualitative estimates of the x-ray intensities. In our program of studies on coordination in hydrated carbonates [2] and phosphates [3], we have refined Harper's structure for $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ using new x-ray data. $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ is the mineral thermonatrite and often occurs with $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (natron) and $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ (trona) [4, 5, 6].

2. Determination of the Structure

Formula: $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. **Unit cell:** Orthorhombic with $a=6.472(2)$ Å, $b=10.724(3)$ Å, $c=5.259(2)$ Å at 24°C as calculated from three pairs of 2θ values of axial reflections from a single crystal and observed on a diffractometer. The standard deviations of the cell parameters are in parentheses and are estimates based on experience with the technique. **Cell volume:** 365.1 Å^3 . **Wavelength used:** 0.710688 Å (Mo $\text{K}\alpha$). **Filter:** 0.025 mm Nb . **Space Group:** $\text{P2}_1\text{ab}$. **Cell contents in formula Wts:** 4. **Equivalent positions:** $x, y, z; 1/2+x, -y, -z; 1/2+x, 1/2-y, z; x, 1/2+y, -z$. **Reciprocal lattice extinctions:** $h0l, h \neq 2n; hk0, k \neq 2n$. **Observed density:** $2.255 \text{ g} \cdot \text{cm}^{-3}$ [7]. **Calculated density:** $2.256 \text{ g} \cdot \text{cm}^{-3}$. **Habit:** Fragment from plate. **Size of crystal:** $\sim 0.35 \text{ mm max.} \sim 0.05 \text{ mm min.}$ **Origin:** Evaporation

of aqueous solution at 60°C . **Linear absorption coefficient:** 4.37 cm^{-1} . **Absorption corrections:** None applied. Maximum error in any intensity from absorption is ~ 10 percent. **Number of reflections:** 2189 were collected from 2 octants and merged into a unique set of 1231 of which 1132 are "observed" reflections and 99 are less than 2σ above background and are "unobserved". **Maximum $\sin \theta/\lambda$ for data:** 0.904 Å^{-1} . **Method used to estimate data:** peak height measurement [8] with a single crystal diffractometer [9] and some peak heights standardized against $\theta/2\theta$ scans. **Scattering factors:** Na, C, O, for neutral atoms given in reference [10]; H from reference [11]. **Least-squares refinements:** Full-matrix, with $\sum (w\|F_o\| - \|F_c\|)^2$ minimized. Refinements include unobserved reflections for which the calculated intensities are more than 2σ above background. **Least-squares weights:** $1/\sigma^2$ normalized so that maximum weight is 1. **Definitions:** counts in peak $= I = P - (T/2T_B)(B_L + B_H)$, $\sigma(I) = (P + (B_L + B_H)(T/(2T_B))^2)^{1/2}$, $F = ((AF)(LP)(I))^{1/2}$, $\sigma(F) = (\sigma(I)/2)(LP/I)^{1/2}$ where P = counts at the peak position, B_L and B_H = background counts at lower and higher 2θ respectively, T = time spent counting peak, T_B = time spent counting each background, AF = attenuator factor, LP = Lorentz polarization correction.

$$R_w = \left(\sum (w\|F_o\| - \|F_c\|)^2 / \sum (w\|F_o\|)^2 \right)^{1/2}$$

$$R = \left(\sum \|F_o\| - \|F_c\| / \sum \|F_o\| \right)$$

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¹Figures in brackets indicate the literature references at the end of this paper.

Final R_w : 0.029. Final R : 0.032. Average shift/error for last cycle: 0.015. Thermal parameters: anisotropic with form

$$\exp \left(-1/4(a^{*2}B_{11}h^2 + b^{*2}B_{22}k^2 + c^{*2}B_{33}l^2 + 2a^*b^*B_{12}hk + 2a^*c^*B_{13}hl + 2b^*c^*B_{23}kl) \right).$$

The structure was refined isotropically from Harper's parameters using the x-ray 67 system [12] of computer programs to $R_w=0.065$; the x parameter of Na(1) was fixed at $x=0$. The structure was refined anisotropically to $R_w=0.044$ and the hydrogens were found unambiguously as the two highest peaks in the difference synthesis in which the coefficients were weighted by the least squares weights. The two next highest peaks were less than 3/4 as high as the peaks assigned to hydrogens and were (a) halfway between C and O(3) in the CO_3 group and (b) 0.7 Å from O(1) of the CO_3 group. The hydrogens were included with variable positional parameters and fixed thermal parameters ($B_H=1 \text{ Å}^2$) in the final refinement to $R_w=0.029$. The largest correlation coefficients are ~ 0.25 between the scale factor and the B_{11} thermal parameters of the two Na ions and ~ 0.15 between these B_{11} thermal parameters. Most correlation coefficients are less than 0.05.

The atomic parameters are given in table 1. The observed and calculated structure factors are given in table 2. The hydrogen positions obtained from the weighted difference synthesis and from the refinements differ by $\sim 0.17 \text{ Å}$. "Calculated" hydrogen positions were derived by applying the geometry of free water ($\text{O—H}=0.958 \text{ Å}$, $\angle \text{H—O—H}=104.5^\circ$) with the constraint that the $\text{O—H} \dots \text{O}$ angles be as near to linear as possible. These hydrogen positions differ from the other positions by about 0.3 Å. The three sets of hydrogen positions are compared in table 3. The distances and angles which involve hydrogen were obtained using the "calculated" hydrogen positions.

3. Description of the Structure

The structure (fig. 1) contains CO_3 anions whose planes are almost perpendicular to a and which form

sheets at $x \sim 0.25$ and $x \sim 0.75$. Because the C atoms lie close to the planes of the a glides, they form columns along a at $y=0.25$, $z \sim 0.60$. Two adjacent CO_3 groups in a column are held together by both being ionically bonded to four Na ions and hydrogen bonded by one water molecule. The four Na ions and the water molecule form a pentagon roughly halfway between the CO_3 sheets. Adjacent CO_3 groups in a given sheet are linked by the Na ions that lie above and below the sheet.

3.1. The Carbonate Anion and Environment

The dimensions in the CO_3 anion are given in table 4 and the environment is detailed in table 4 and figure 2. The CO_3 group is nearly trigonal. As can be seen in figures 1 and 2, O(2) is the only oxygen which is not hydrogen bonded, being instead ionically bonded to four Na ions. The absence of hydrogen bonding to O(2) may account for the observation that the C—O(2) bond is apparently the shortest of the three. O(1) is coordinated to three Na ions and is the acceptor in the hydrogen bond $\text{O(1)} \dots \text{H(1)—O(4)}$ from the water molecule. O(3) is bonded strongly to two Na ions and more weakly (2.822 Å) to a third Na(2). O(3) is the acceptor in the hydrogen bond $\text{O(3)} \dots \text{H(2)—O(4)}$ from the water molecule.

Since the planes of the CO_3 groups are all essentially perpendicular to a , this is expected to be the direction of lowest refractive index, as was found by Harper [1]. Later workers [13, 14] apparently did not permute the refractive indexes when they permuted the unit cell axes to fit crystallographic convention.

3.2. The Sodium Environments

The two crystallographically distinct Na ions in the structure are in general positions. Their environments are shown in figure 3 and are given in table 5.

Na(1) is bonded ionically to five oxygens from CO_3 groups, and strongly to one water oxygen. Four of the CO_3 oxygens, O(1), O(2'), O(3), O(3'), figure 3, define an approximate square about Na(1), and water oxygen O(4) forms the apex of a square pyramid. The fifth carbonate oxygen, O(2), is in the same CO_3 group as O(1); the CO_3 group is therefore coordinated edgewise to Na(1). The position of O(2) is such that the coordina-

TABLE 1. Atomic parameters of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$

Atom	x	y	z	B_{11}^*	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Na(1)	0.0000	0.1938(1)	0.1398(1)	1.40(3)	1.54(3)	1.36(3)	0.17(3)	0.17(3)	0.08(2)
Na(2)	.0651(2)	.0020(1)	-.3786(2)	1.44(3)	1.19(3)	1.76(3)	.31(2)	.25(3)	.09(3)
C	-.2151(3)	.2556(2)	.6025(3)	.45(6)	1.11(6)	1.17(5)	-.06(5)	-.05(5)	-.03(5)
O(1)	-.2010(3)	.1381(1)	.5457(3)	1.56(6)	0.72(5)	2.72(7)	.08(5)	-.15(6)	-.47(4)
O(2)	-.2027(3)	.3369(1)	.4267(2)	1.73(6)	1.27(5)	1.24(5)	-.05(5)	-.04(5)	.47(4)
O(3)	-.2398(3)	.2876(1)	-.1639(2)	1.42(6)	2.14(6)	0.90(4)	-.28(5)	.25(4)	-.32(4)
O(4)	.0325(3)	-.0296(1)	.0683(3)	1.64(7)	1.43(6)	1.92(6)	-.21(5)	-.25(5)	.39(4)

Figures in parentheses are standard errors in last significant figure quoted, and were computed in the final cycle of full-matrix least-squares refinement.

*Thermal parameters are in Å^2 .

a

^a The columns are k , $10F_o$, $10F_c$. "Unobserved" reflections are marked by *. F_o and F_c are on an absolute scale.

TABLE 3. *The hydrogen positions in Na₂CO₃·H₂O*

* Assuming the geometry of free water with $\text{O—H} = 0.958 \text{ \AA}$ and $\angle \text{H—O—H} = 104.5^\circ$, and making the $\text{O—H} \cdots \text{O}$ hydrogen bonds as linear as possible.

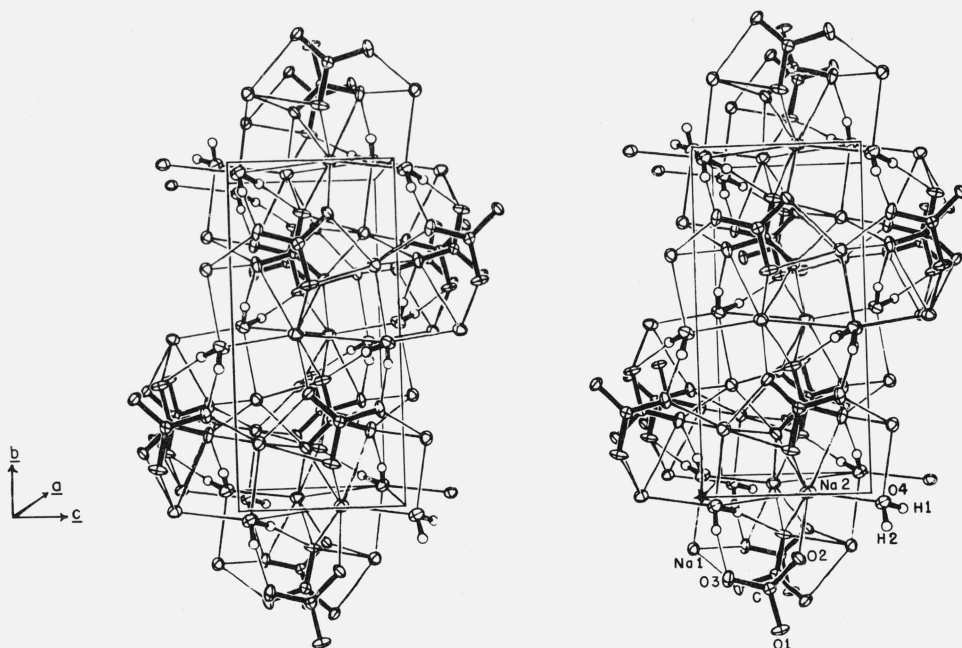


FIGURE 1. A stereoscopic illustration of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ viewed along *a*.
The origin of the unit cell is marked by the asterisk.

TABLE 4. The CO_3 group

Atoms	Distances, Å, or angle, deg.
C, O(1).....	1.299(3)
C, O(2).....	1.274(2)
C, O(3).....	1.285(2)
O(1), O(2).....	2.223(2)
O(1), O(3).....	2.229(2)
O(2), O(3).....	2.230(2)
O(1), C, O(2).....	119.6(2)
O(1), C, O(3).....	119.2(2)
O(2), C, O(3).....	121.2(2)
O(1), Na(1).....	2.570(2)
O(1), Na(2).....	2.293(2)
O(1), Na(2').....	2.307(2)
O(1), O(4).....	2.907(2)
O(1), H(1).....	1.96
O(2), Na(1).....	2.521(2)
O(2), Na(1').....	2.468(2)
O(2), Na(2').....	2.508(2)
O(2), Na(2).....	2.491(2)
O(3), Na(1).....	2.444(2)
O(3), Na(1').....	2.330(2)
O(3), Na(2).....	2.822(2)
O(3), O(4).....	2.685(2)
O(3), H(2).....	1.74

In all tables of interatomic distances and angles, the quantities in parentheses are standard errors in the last significant figure and were computed from the standard errors in the atomic positional parameters and in the cell parameters. The primes refer to atoms in figure 2.

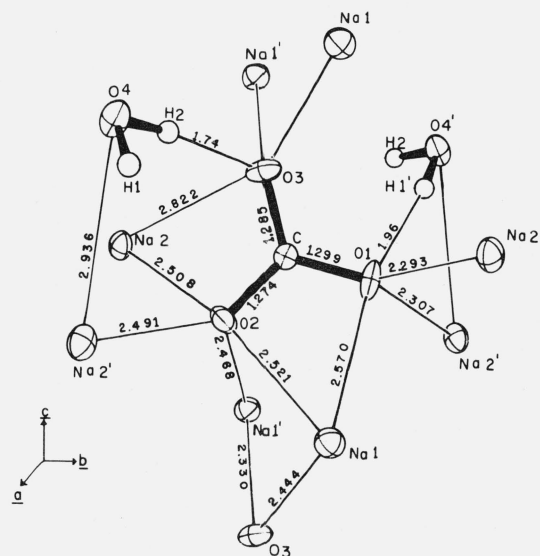


FIGURE 2. The carbonate group environment in $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$.
The primes refer to atoms in table 4.

tion about Na(1) cannot be considered octahedral. The next oxygen in the direction of the octahedral apex is the water oxygen O(4'), which is relatively far (3.669 Å) from Na(1).

The coordination of Na(2) is similar to that of Na(1). Na(2) is slightly displaced from the center of an approximate square of carbonate oxygens, O(1'), O(2''), O(1''), O(2''). The displacement is towards the strongly bonded water molecule O(4), which is the

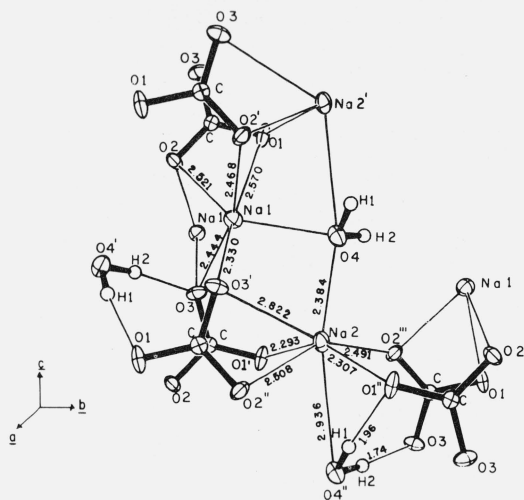


FIGURE 3. The water and sodium environments in $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. The primes refer to atoms in tables 5 and 6.

TABLE 5. The sodium environments

Atoms	Distance, Å
Na(1), O(1).....	2.570(2) Å
Na(1), O(2).....	2.521(2)
Na(1), O(3).....	2.444(2)
Na(1), O(4).....	2.434(2)
Na(1), O(2').....	2.468(2)
Na(1), O(3').....	2.330(2)
Na(1), O(4').....	3.669(2)
Na(2), O(4).....	2.384(2) Å
Na(2), O(1').....	2.293(2)
Na(2), O(1'').....	2.307(2)
Na(2), O(2'').....	2.508(2)
Na(2), O(2'').....	2.491(2)
Na(2), O(4'').....	2.936(2)
Na(2), O(3').....	2.822(2)

The primes refer to the atoms in figure 3.

apex of a square based pyramid (base down in figure 3). The coordination of Na(2) is completed by O(4'') (2.936 Å) which is the remaining apex of an approximate octahedron, and by O(3') which is in the same CO_3 group as O(2''). Thus the CO_3 group is coordinated edgewise to Na(2) also, this time using O(2) and O(3) instead of O(1) and O(2), which are used to coordinate to Na(1). This edgewise coordination is shown in figure 2. The coordination to Na(2) comprises five carbonate oxygens and two water molecules instead of four carbonate oxygens and two water molecules as suggested by Harper [1] and noted by Wells [15].

3.3. The Water Environment

The water environment is given in table 6 and shown in figure 3. The water molecule is bonded to Na(1)

and Na(2) with distances of 2.434 and 2.384 Å respectively, and forms hydrogen bonds to oxygens O(1) and O(3) of neighboring CO_3 groups. Na(1), Na(2), O(1), and O(3) are arranged approximately tetrahedrally about the water oxygen. The distortion of this tetrahedron is considerable as can be seen from the angles listed in table 6. The closest H . . . Na distance is H(1) . . . Na(2)=2.42 Å, which is in the normal range.

TABLE 6. The water environment

Atom	Distance Å or angle, deg.
O(4),Na(1)	2.434(2) Å
O(4),Na(2)	2.384(2)
O(4),Na(2')	2.936(2)
O(4),O(1)	2.907(2)
O(4),O(3)	2.684(2)
H(1),O(1)	1.96
H(2),O(3)	1.74
Na(1),O(4),Na(2)	91.15(6)°
O(1),O(4),Na(1)	109.70(7)
O(1),O(4),Na(2)	133.83(9)
O(3),O(4),Na(1)	129.28(9)
O(3),O(4),Na(2)	110.29(7)
O(1),O(4),O(3)	88.12(6)
O(4),H(1),O(1)	168.
O(4),H(2),O(3)	167.

The prime refers to an atom in figure 3.

The calculated hydrogen positions in table 3 were obtained using the geometry of free water and imposing the condition that the O—H . . . O angles both be as linear as possible. Because H(2) . . . O(3) is shorter (1.74 Å) than H(1) . . . O(1) (1.96 Å) it is possible that the hydrogen bond O(4)—H(2) . . . O(3) is strictly linear. Assuming the same water geometry, the hydrogens would then be ≈ 0.14 Å away from the positions given in table 3 at 0.145, -0.046, 0.182 for H(1) and -0.065, -0.095, 0.102 for H(2). The O(4)—H(1) . . . O(1) angle would then be 156° , and the H(1) . . . O(1) and H(2) . . . O(3) distances would be 2.01 Å and 1.73 Å, respectively. The closest H . . . Na distance would be H(1) . . . Na(2)=2.39 Å.

Collection of the diffractometer data was made possible through the cooperation of E. C. Prince. The x-ray 67 system of computing programs (J. M. Stewart, University of Maryland, Editor) was used for most calculations. We thank Joy S. Bowen and Pamela B. Kingsbury for technical help.

This investigation was supported in part by research grant DE-00572-09 to the American Dental Association from the National Institute of Dental Research and is part of the dental research program conducted by the National Bureau of Standards, in cooperation with

the Council on Dental Research of the American Dental Association; the United States Army Medical Research and Development Command; the Dental Sciences Division of the School of Aerospace Medicine, USAF; the National Institute of Dental Research; and the Veterans Administration.

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(Paper 74A3–603)